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Optimal separation of phenol from model oils by forming deep eutectic solvents with quaternary ammonium salts

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Abstract–Various quaternary ammonium salts are used to separate phenol from model oil by forming deep eutectic solvents (DESs). The results indicate that the types of quaternary ammonium salt ions and the molecular symmetry of quaternary ammonium have obvious influence on recovery for phenol. Tetraethylammonium chloride (TEAC), which contains suitable ions and symmetry reveals highest phenol recovery in the model oil. The separation mechanism is discussed and the structures of DESs (TEAC/Phenol) are proved on Fourier transform infrared transform (FTIR). To recycle TEAC, diethyl ether is used as anti-solvent to precipitate TEAC from TEAC/Phenol system. The structure of regeneration TEAC is proved on FTIR and ^{1}H NMR. The recovery for phenol is decreased from 97.45% to 14.30% with the increase of regeneration times. The optimal separation condition was obtained by response surface methodology at 30 °C (separation temperature) for 40 min (separation time) with 3.75 g TEAC (mass of TEAC) in 10 mL model oil (phenol recovery: 99.3%). In contrast to the traditional methods to separate phenol, this proposed method avoids the use of alkalis and acid, and with less effluent.

Keywords: Deep Eutectic Solvents, Separation, Phenol

INTRODUCTION

Phenol, one of the basic materials for the organic chemical industry, is used to produce synthetic fibers, engineered plastics, pesticides, medicines, preservatives and other products [1]. Most phenol is derived from coal liquefaction oil, coal tar and petroleum [2]. Therefore, it is necessary to find improved methods for separating phenol from oils before further application. The conventional method to separate phenol from oil mixtures is chemical extraction using aqueous alkaline solutions (such as aqueous NaOH) and then acidification of the extract by mineral acids (such as aqueous H_2SO_4) to increase the recovery of the phenol [3]. The disadvantages of this method are the large use of both strong alkalis and acids. The processes also produce excessive amounts of waste water containing phenol. So, a green and efficient method to separate phenol from oil mixtures using a non-aqueous method was investigated.

Deep eutectic solvents (DESs) used for separation have received intense interest due to their environmental properties [4-6]. In 2003, DESs were developed by Abbott et al., which were generally composed of hydrogen bond acceptors (HBAs), such as quaternary ammonium salts and hydrogen bond donors (HBDs). Phenol can be used as HBD to form DESs with quaternary ammonium salts. DESs are a eutectic mixture for which the melting point is lower than that of each individual component. Some DESs have the same physical properties and phase behavior as ionic liquids. The ease of synthesis and availability makes these DESs versatile alternatives to ionic liquids, as reviewed in the literature [7-9]. These DESs have been proposed for applications such as electrodeposition [10], electropolishing [11], organic synthesis [12] and extraction processing [13,14]. Various quaternary ammonium salts used to separate phenol by forming DESs is viable method in the model oil (containing phenol) [15]. Compared with present industrial extraction methods, this non-aqueous deep eutectic solvent separation process could avoid the use of alkali and acid, and reduce the size of the separator [16].

To obtain improved separation effects, optimizing the separation process is necessary. Response surface methodology (RSM) is an effective tool for optimizing a range of processes where many factors and interactions affect the desired response [17]. Box-Behnken design (BBD) is one type of RSM, which explores the relationships with several explanatory variables and one or more response variables [18]. When many factors and interactions affect the desired response, Box-Behnken (BBD) is an effective tool for optimizing the process. The main advantage of BBD is to reduce the number of experimental trials needed to evaluate multiple variables and their interactions. Therefore, it is less laborious and time consuming than other approaches requiring optimizing a process. It finds the optimal prediction of response values and the corresponding experimental conditions between the multivariate regression equation fitting each factor and response values. So, when we choose the model of BBD to optimize the method recovery, the 17-tests which can replace the three single-factor tests (need 27-tests) have been confirmed by BBD model. It has been successfully applied in many fields, such as optimal of the extraction condition [19-22].

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In this study, a range of quaternary ammonium salts were used to separate phenol from model oil composed of toluene. The effect factors of the recovery were studied by structures of quaternary ammonium salts, such as the types of cation and anion, and the symmetry of the quaternary ammonium salts. The separation mechanism was discussed and the best separation effect of quaternary ammonium salt was proved on Fourier transform infrared transform (FTIR) and ^{1}H NMR. The quaternary ammonium salts recycle process was investigated in this experiment. In the separation process, such as separation temperature, separation time and added mass of quaternary ammonium salt were also optimized systematically by RSM.

EXPERIMENTAL

1. Reagents and Standards

Phenol, ammonium chloride (NH_4Cl), ammonium bromide (NH_4Br), tetramethylammonium chloride (TMAC), tetramethylammonium bromide (TMAB), tetraethylammonium chloride (TEAC), tetraethylammonium bromide (TEAB), methyltriethylammonium chloride (MTAC), tetrapropylammonium chloride (TPAC), tetrapropylammonium bromide (TPAB) and choline bromide (ChBr) were purchased from Heowns Co., Ltd. (Tianjin, China). Choline chloride (ChCl) was obtained from Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Diethyl ether and toluene were acquired from Tianjin Chemical Reagent Co., Ltd. (Tianjin, China). Methanol was bought from Concord Chemical Research Institute (Tianjin, China). Potassium bromide (KBr) was obtained from Hengshan Chemical Reagent Co., Ltd. (Tianjin, China). Ultrapure water was bought from Hangzhou Wahaha Group Co., Ltd. (Hangzhou, China), and all the samples were filtered through a 0.45 μm nylon membrane before injecting into the high performance liquid chromatography (HPLC) system.

2. Apparatus and HPLC Analysis

The spectra of samples were analyzed on VERTEX70 FTIR (Bruker, Germany) at 4,000-400 cm^{-1}. The molecular structure of samples was analyzed on ^{1}H NMR (Bruker-400 MHz, Germany). The chromatography system consisted of a LC-10ATVP pump and SPD-10AVP UV-VIS detector (Shimadzu, Kyoto, Japan) with an injector (10 μL sample loop). The analysis was performed on an Optima Pak C_{18} column (5 μm, 150×4.6 mm, RS tech Corporation, Daejeon, Korea) and Chromatography Data System N2000 (Surwit Technology, Hangzhou, China). The mobile phase was methanol/water (30/70, v/v) and flow rate was set at 0.8 mL/min. The wavelength of the detector was set at 270 nm with injection volume 10 μL [23]. The linearity of the analytical method was evaluated by a calibration curve at five concentration levels of phenol standard solutions, ranging from 0.5-100.0 μg/mL. For assessing the accuracy, the recoveries of the non-spiked samples and the samples spiked with phenol (5.0, 50.0, 100.0 μg/mL) were measured using the established method (n=3).

3. Preparation of Model Oil and Separation Process

Model oil was prepared by adding 50.0 g phenol into the volumetric flask (250 mL) and constant volume by toluene (concentration of phenol: 0.2 g/mL). In a typical experiment, a mass of quaternary ammonium salt (the mole ratio of salt/phenol: 1/1) as separation media was added to 10 mL model oil (contain 21 mmol phenol) in 25 cm^3 glass tube. The glass tube was partly immersed in a water bath that was set at the desired temperature (40 °C) and was magnetically stirred. After stirring for separating 40 min, the two phases were allowed to settle for more than 30 min. A small amount of sample from the upper oil phase was taken and analyzed on HPLC to determine its composition. Then the quaternary ammonium salt which had best recovery was used in the next experiment.

4. FTIR and ^{1}H NMR Analysis

The samples were characterized on FTIR with KBr pellet method. FTIR discs process: 1 mg sample (Phenol, TEAC and regenerated TEAC) was ground together with 200 mg KBr for tablets, respectively, and the DESs (TEAC/Phenol) were smeared on KBr tablets evenly. The percent of sample to KBr was 0.5%. The wave numbers of FTIR measurement range were controlled from 4,000 to 400 cm^{-1}. Molecular structure of samples (TEAC and regenerated TEAC) was obtained on ^{1}H NMR (400 MHz). TEAC and regenerated TEAC were in an equivolume mixture of $CDCl_3$.

5. The Procedure of Recycling TEAC

In this work, diethyl ether was an efficient solvent to recover TEAC from the DESs (TEAC/Phenol). The typical recycling process was as follow: 3.48 g (21 mmol) of TEAC was added to 10 mL model oil (contain 21 mmol phenol) with an initial phenol content of 0.2 g/mL at 40 °C. The mixture was magnetically stirred for 30 min, and settled for 30 min. The model oil and DESs (TEAC/Phenol) were obviously layered and separated. At first, the model oil phase was removed from the glass tube and 25 mL of diethyl ether was added as an anti-solvent to the TEAC/Phenol phase with shaking. After this process, TEAC was recrystallized quickly and precipitated at the bottom of the separator glass tube. Then the diethyl ether -Phenol and re-crystallized TEAC was separated by suction filtration. The re-crystallized TEAC was dried under vacuum at 80 °C for at least 2 h to remove a small amount of dissolved model oil and diethyl ether until the TEAC mass was constant. Finally, the regenerated TEAC was investigated on FTIR and ^{1}H NMR. To investigate the phenol method recovery of regenerated TEAC, regenerated TEAC was studied with the same typical process for the next cycle.

6. Optimization of Separation Process by RSM

After determining the preliminary range of method recovery through a single-test, we used a BBD with three independent variables. The separation time (X_1), separation temperature (X_2) and mass of TEAC (X_3) were the independent variables selected to be optimized for the recovery of phenol in the model oil. The appropriate range of the three variables was determined based on single-factor experiment. The phenol method of recovery (Y) was taken

Table 1. Independent variables and their levels used for BBD

Variables	Level		
	−1	0	1
Separation time (X_1) (min)	20	40	60
Separation temperature (X_2) (°C)	30	40	50
Mass of TEAC (X_3) (g)	1	2.5	4

as the response of the design experiments. Table 1 lists the coded and uncoded levels of the independent variables. The experimental runs were randomized to minimize the effects of the unexpected variables in the observed responses. The three test variables were coded according to the following equation:

$$x_i = \frac{X_i - X_0}{\Delta X} \quad i=1, 2, 3 \tag{2}$$

In this equation, x_i is the coded value of the independent variable, X_i is the actual value of the independent variable; X_0 is the actual value of the independent variable at the center point; and ΔX is the step change value of the independent variable. A second-order polynomial model was fitted to correlate the relationship between the independent variables and the response (phenol recovery) to predict the optimized conditions.

$$Y = A_0 + \sum_{i=1}^{3} A_i X_i + \sum_{i=1}^{3} A_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=1+1}^{3} A_{ij} X_i X_j \tag{3}$$

In this equation, Y is the dependent variable (phenol recovery), A_0 is a constant, and A_i, A_{ii} and A_{ij} are coefficients that were estimated by the model. X_i and X_j are the levels of the independent variables that represent the linear, quadratic and cross-product effects of the X_1, X_2 and X_3 factors on the response, respectively. The model evaluated the effects of each independent variable on the response. The experimental design was analyzed and the predicted data were calculated by using the Design-Expert software (v.7.1.6, Stat-Ease, Inc., Minneapolis, USA) to estimate the response of the independent variables. Subsequently, three additional experiments were conducted to verify the validity of the statistical experimental strategies.

RESULTS AND DISCUSSION

1. Effect of Quaternary Ammonium Salt Structures

1-1. Effect of Cation on Recovery

The processes to separate phenol by NH_4Cl, TMAC, TEAC, TPAC, NH_4Br, TMAB, TEAB and TPAB were carried out at 40 °C for 40 min (Fig. 1). The results showed that the different cations of quaternary ammonium salts had significant change on phenol method of recovery. The phenol recovery with different cations followed the order: $[TEAC]^+ > [TPAC]^+ > [TMAC]^+ > NH_4^+[Cl]^-$, $[TEAB]^+ > [TPAB]^+ > [TMAB]^+ > NH_4^+[Br]^-$. NH_4Cl and NH_4Br still kept lot soild state, which meant the two quaternary ammonium salts cannot interact with phenol in the model oil phase. Due to the low enthalpy of formation of the eutectic mixture, there was no hydrogen bond formation between the anions ($[Cl]^-$ and $[Br]^-$) and the OH group on phenol, respectively. When TMAC, TEAC, TPAC were added to the model oil, a eutectic phase was observed immediately. The concentrations of phenol in the oil were decreased greatly by using TMAC, TEAC and TPAC, and the phenol separation efficiency was 70.10%, 97.45% and 90.23%, respectively. TEAC showed the highest recovery. The same separation condition was applied in TMAB, TEAB and TPAB. TEAB (83.62%) showed the better recovery than TMAB (65.30%) and TPAB (80.39%).

The results showed that the suitable linear alkyl chain length of the quaterary ammonium cation can improve the phenol recovery in the model oil. With the incresing of linear alkyl chain length on cations, the interaction of cations and anions was weak. So there was an optimum distance between the canions and anions for hydrogen bond formation. NH_4Cl and NH_4Br showed a close distance between cations and anions, so that the intramolecular interaction was too strong to form DESs. TMAC, TEAC, TPAC, TMAB, TEAB and TPAB had large cations, and the distance between the cations and anions was sufficient to produce lower intramolecular interaction between the cations and anions. Thus the space was sufficient for the phenol to interact with cations to form DESs. But TPAC and TPAB showed the weaker recovery than TEAC and TEAB, respectively. Because TPAC and TPAB had too long alkyl chain lengths, it increased the interaction between toluene and salts. So TEAC and TEAB had the suitable alkyl chain.

1-2. Effect of Anion on Recovery

The effect of anion on phenol recovery showed that chloride-

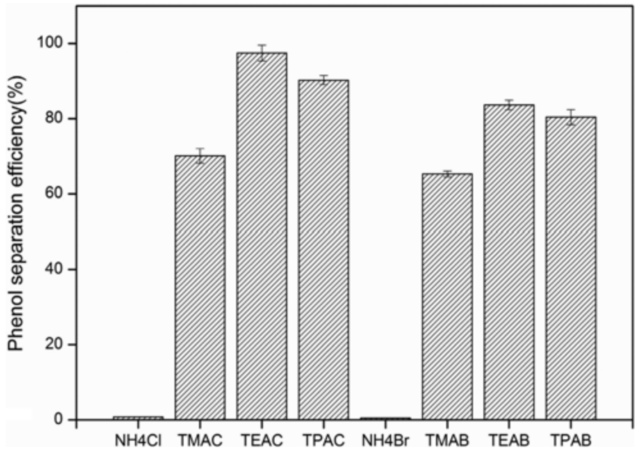

Fig. 1. The phenol method of recovery by quaternary ammonium salt with different cations from model oil (initial phenol content: 0.2 g/mL; separation temperature: 40 °C; separation time: 40 min; mole ratio of salt/phenol: 1/1).

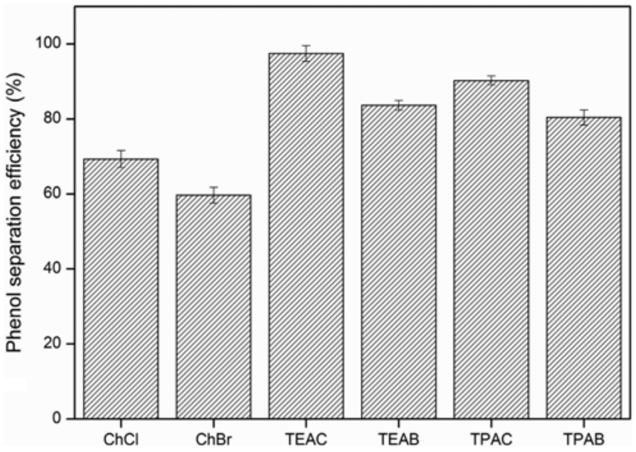

Fig. 2. The method of recovery of phenol by quaternary ammonium salt with different anions from model oil (initial phenol content: 0.2 g/mL; separation temperature: 40 °C; separation time: 40 min; mole ratio of salt/phenol: 1/1).

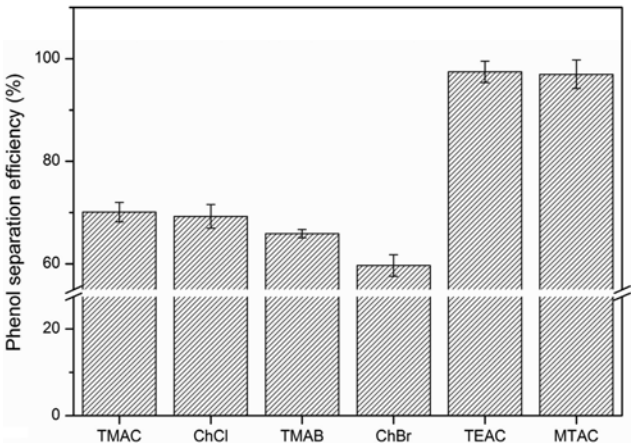

Fig. 3. The method of recovery of phenol by quaternary ammonium salt with asymmetric and symmetric structures from model oil (initial phenol content: 0.2 g/mL; separation temperature: 40 °C; separation time: 40 min; mole ratio of salt/phenol: 1/1).

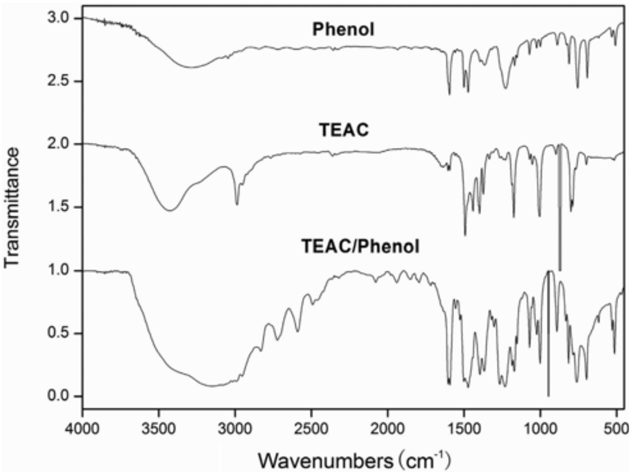

Fig. 4. FTIR spectra of phenol, TEAC, and DES (TEAC/Phenol).

based quaternary ammonium salts showed greater recovery than bromine-based quaternary ammonium salts in Fig. 2. For instance, phenol separation efficiencies by using ChCl, TEAC were 69.28%, 97.45%, while the separation efficiencies were 59.69% and 83.62% by using ChBr and TEAB. Because the chloride ion had larger electronegativity and stronger interaction with OH group on phenol than bromine ion.

1-3. Effect of Symmetry on Recovery

Fig. 3 shows the symmetry of the quaternary ammonium cations on the phenol separation efficiencies which followed the order: TMAC>ChCl, TMAB>ChBr and TEAC>MTAC. The phenol separation efficiencies of quaternary ammonium salts with symmetric cations were higher than asymmetric cations. The symmetric cations had a stiffer intermolecular potential than the asymmetric cations [24,25]. For instance, MTAC (96.97%) had a lower symmetry than TEAC (97.45%). MTAC exhibited anisotropic motion, which led to an uneven distribution of electric charge and a weaker interaction between the cation and anion than TEAC. The results showed that asymmetric structures were not conducive to enhance phenol recovery.

Through the above experiment, the structure of quaternary ammonium had a significant effect to separate phenol. The results showed that TEAC had the optimal recovery. Because TEAC showed the suitable linear alkyl chain length of the quaterary ammonium salt (sufficient space to interact with phenol), the larger electronegativity chloride ion (the stronger electrostatic force to interact with phenol), and the high symmetry cation (electric charge distribution more uniform). These characteristics of TEAC endowed the better recovery than other quaternary ammonium salts.

1-4. The Mechanism for Separating Phenol by Forming DESs

In summary, the coordinating role of the cations and anions of quaternary ammonium salt was the main factor to influence the phenol recovery. Remarkably, the halide-based quaternary ammonium salt played an important role for separating phenol from model oil phase to eutectic phase. Because the halide anion can form the hydrogen-bonding with phenol and the recovery was based on the strength of hydrogen-bongding interaction. FTIR was used to prove the hydrogen-bonding information (Fig. 4). The ν-OH stretching vibration of pure phenol was observed at 3,421 cm^{-1}, which shifted to 3,148 cm^{-1} in DESs (TEAC/Phenol). The FTIR of phenol in the DESs showed a change in the vibrational states because portion of the cloud of electrons of the oxygen atom transferred to the hydrogen bonding, resulting in a smaller force constant. Thus, the shift of the ν-OH stretching vibration suggests the existence of hydrogen-bonding between phenol and TEAC when the DESs was formed.

2. Structure Analysis and Reuse of Regenerated TEAC

In this work, diethyl ether was used as an efficient anti-solvent to separate phenol and TEAC from the DESs. After separation, the regeneraed TEAC was identified on FTIR and The spectra of fresh TEAC and regenerated TEAC were observed with the same group (Fig. 5). Fig. 6 shows the ^{1}H NMR spectrum of TEAC and regenerated TEAC in $CDCl_3$. In this system, TEAC and regenerated TEAC were observed with the same hydrogen signal (1.20-1.24 ppm and 3.30-3.35 ppm, respectively). The results showed that the structure of regenerated TEAC was not changed. The phenol method of using regenerated TEAC and the mass of regenerated TEAC are shown

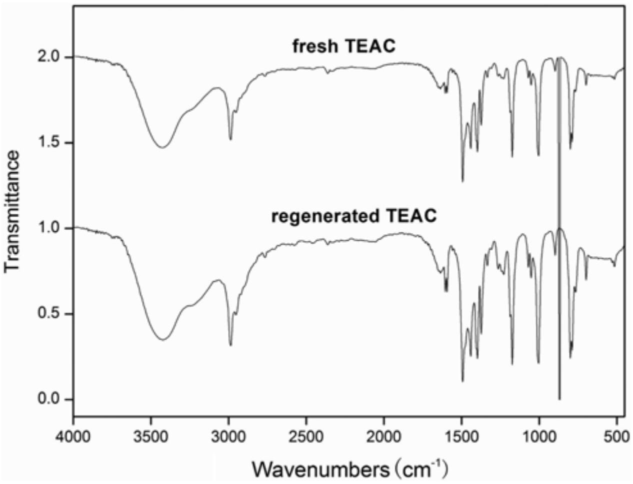

Fig. 5. FTIR spectra of fresh TEAC, and regenerated TEAC.

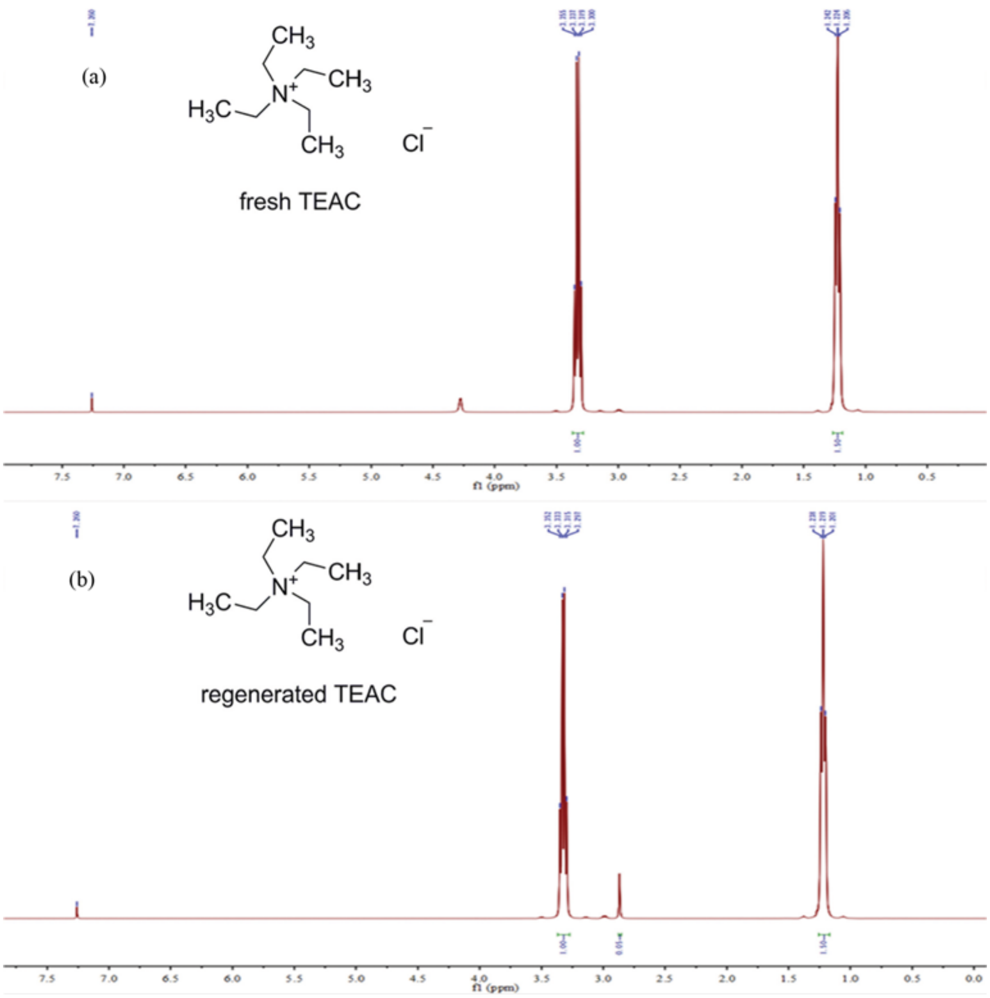

Fig. 6. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of (a) fresh TEAC, (b) regenerated TEAC.

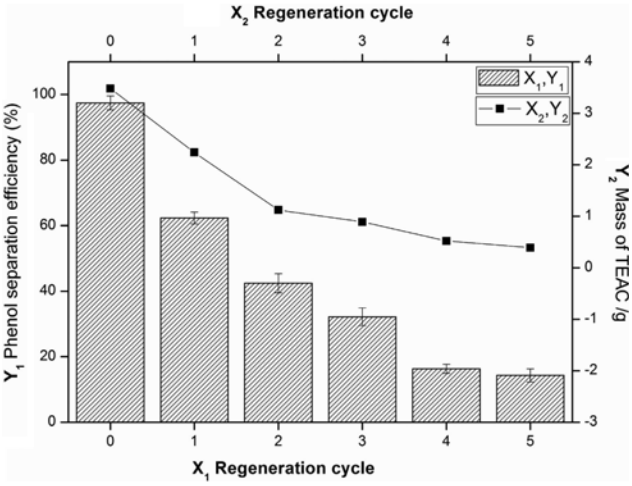

Fig. 7. The method recovery of phenol and regeneration mass of TEAC with regeneration cycle.

in Fig. 7. The mass of original TEAC was 3.48 g, and the masses of regenerated TEAC were sequentially 2.24 g, 1.12 g, 0.89 g, 0.52 g and 0.39 g. The phenol recovery was 97.45% for the original sample of TEAC and those using regenerated TEAC from one time to five times were sequentially 62.34%, 42.45%, 32.21%, 16.30% and 14.30%, respectively. The results showed that TEAC can be reused many times and still have a certain effect for separating phenol. But the recovery was decreased with the increase of regeneration times. Because TEAC and phenol form strong hydrogen bonding force, it would make TEAC hard to completely recycle from model oil.

3. Optimization of the Separation Conditions by RSM

3-1. Regression Models of Response

To obtain a more realistic mode, it was necessary to examine the process variables. After determining the preliminary range of recovery through a single-test, a BBD with three independent variables was employed. The related data is shown in Table S1. Separation time (X_1): the diffusion of phenol was essential in the separation process, so the change of reaction time can affect the diffusion efficiency. With the changing of reaction time, the diffusion efficiency of components and mass transfer for phenol were changed. Separation temperature (X_2): With the changing of temperature, the solubility of components was changed. These results would have some influence on phenol separation. Mass of TEAC (X_3): With the changing of mass of TEAC, the molar ratio between TEAC and phenol was changed. A large TEAC amount was an unnecessary waste, whereas a smaller amount would make the phenol separation incomplete. So, considering the economic efficiency and recovery, the mass of TEAC should be optimized. Therefore, preliminary trials were performed to determine the range of percentages of separation time (20-60 min), separation temperature (30-50 °C) and mass of TEAC (1-4 g).

To optimize the separation conditions of the phenol in model oil, a 17-run BBD with three variables (separation time, separation temperature and mass of TEAC) and three levels (Table 1) was used to fit a second-order response surface, and the phenol recovery was taken as the response (Table 2). The predicted values of the responses were obtained from a quartic model by fitting the experimental data to the following Eqs. (3):

$$Y=94.28-0.43X_1+4.25X_2+17.25X_3+0.11X_1X_2+0.53X_1X_3 -8.62X_2X_3-6.21X_1^2+8.53X_2^2-14.71X_3^2 \quad (3)$$

where Y is the predicted response (phenol method recovery); X_1, X_2 and X_3 are separation time (min), separation temperature (°C) and mass of TEAC (g), respectively. The model BBD was used to find the dynamic effect between three factors more than one factor tendency. According to Fig. S1, we can find that with the changing of temperature and time, the recovery was changed only from 90% to 95%. The results indicated that with the change of temperature and time, the change of recovery was not obvious. In Fig. S2 and Fig. S3, according to these data, we can find that with the changing of the amount of TEAC, the recovery was changed from 60% to 90% and 60% to 100%. The results showed that amount of TEAC will strongly affect the recovery. It will provide enough TEAC to react with phenol and optimize the suitable mass to avoid unnecessary waste. According to Fig. S1-3, the amount of TEAC affects the method recovery obviously. The reaction time and temperature only have a little influence on the separation process.

The significance of each coefficient was checked by using the *F*-test and the *p* value (Table 3). The *p* value was used as a tool to check the significance of each coefficient, and it indicated the interaction strength between each independent variable. The ANOVA of the quadratic regression model demonstrated that the model was highly significant, with a very low probability value ($p<0.0001$). The model *F*-value of 5.50 implied that the model was not significantly relative to the noise, and there was only a 1.75% chance that a model F-Value that was this large occurred because of noise. The lack of fit F-value of 6775.35 implied the lack of fit was significant, and there was a 0.01% chance that a lack of fit *F-value* could have occurred because of noise. The regression coefficients and the corresponding *p* values are also shown in Table 3. The *p* values of each model confirmed that the four coefficients (X_1, X_2, X_3, $X_1\times X_1$) were all significant. Therefore, separation time, separation temperature

Table 2. Box-Behnken experimental designs of the independent variables

Run	X_1	X_2	X_3	Phenol method recovery	
				Actual values	Predicted values
1	20	50	2.5	96.54	88.50
2	40	40	2.5	94.33	94.28
3	40	40	2.5	94.22	94.28
4	20	30	2.5	96.85	92.89
5	40	40	2.5	94.46	94.28
6	60	30	2.5	96.45	91.81
7	40	40	2.5	94.38	94.28
8	20	40	1	49.98	57.07
9	40	40	1	64.02	74.28
10	40	50	1	75.44	83.72
11	40	30	1	61.13	57.98
12	60	40	1	47.39	55.15
13	20	40	4	98.27	90.51
14	60	40	4	97.81	90.71
15	40	50	4	97.84	100.98
16	60	50	2.5	96.58	100.53
17	40	30	4	98.00	109.72

X_1: separation time; X_2: separation temperature; X_3: mass of TEAC

Table 3. Analysis of variance of the experimental results of the BBD

Variables	Sum of squares	DF	Mean square	*F* value	*p*-Value Prob.>*F*
Model	4170.83	9	463.43	5.50	0.0175
A-separation time	1.45	1	1.45	0.017	0.8992
B-separation temperature	144.25	1	144.25	1.17	0.2321
C-mass of TEAC	2379.81	1	2379.81	28.24	0.0011
AB	0.048	1	0.048	0.00057	0.9816
AC	1.13	1	1.13	0.013	0.9109
BC	297.05	1	297.05	3.52	0.1026
A^2	162.30	1	162.30	1.93	0.2078
B^2	306.47	1	306.47	3.64	0.0982
C^2	911.21	1	911.21	10.81	0.0133
Residual	589.98	7	84.28		
Lack of fit	589.86	3	196.62	6775.35	<0.0001
Pure error	0.12	4	0.029		
Cor total	4760.81	16			

Table 4. Analysis of variables for the fitted quadratic polynomial model of phenol method of recovery

Item	Std. Dev.	Mean	C.V. %	Press	R^2	R^2_{Adj}	R^2_{Pred}	Adeq. precision
Value	9.18	88.45	10.38	9437.98	0.8761	0.7167	N/A	7.749

and mass of TEAC were important factors for removing phenol from model oil.

The coefficient of determination (R^2=0.8761), the adjusted coefficient of determination (R^2_{Adj}=0.7167) and the coefficient of variation (C.V.=10.38%) are shown in Table 4. These values indicated that the accuracy and the general availability of the polynomial model were adequate. A negative R^2_{Pred} implied that the overall mean was a better predictor of our response than the current model. *Adeq. Precision* measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 7.749 indicated an adequate signal. This model can be used to navigate the design space.

3-2. Optimizing the Separation Conditions

The separation conditions were optimized by obtaining the selected variables using software with the regression equation. The 3D response surfaces were provided as graphical representations of the regression equation.

As shown in Fig. 8(a), when the mass of TEAC was fixed to 2.50 g, with increasing separation time, the phenol recovery increased until a separation time of 40 min. This meant that there was about 40 min for mass transfer for phenol. Fig. 8(b) shows that the mass of TEAC had a larger effect on the phenol recovery than temperature. In Fig. 8(c), the mass of TEAC also had a large effect on the phenol recovery than separation time, because the mass of TEAC provided enough HBA to form DESs (TEAC/Phenol).

The separation conditions (X_1=40 min, X_2=31.4 °C and X_3=3.75 g) were optimized by using the model equation by solving a regression equation with the estimated recovery of 100.918%. These predicted conditions were used to separate phenol and test the prediction from the model. Under these optimized conditions (X_1=40 min, X_2=30 °C and X_3=3.75 g), 99.3% phenol was separated, confirming that the response model was suitable for optimization.

4. Analytical Performance

A series of experiments were performed to determine the linearity, precision, detection limit and other characteristics of the method under the optimized condition. Phenol showed good linearity from 0.5 to 100.0 μg/mL with correlation coefficients (R^2=0.9995). The

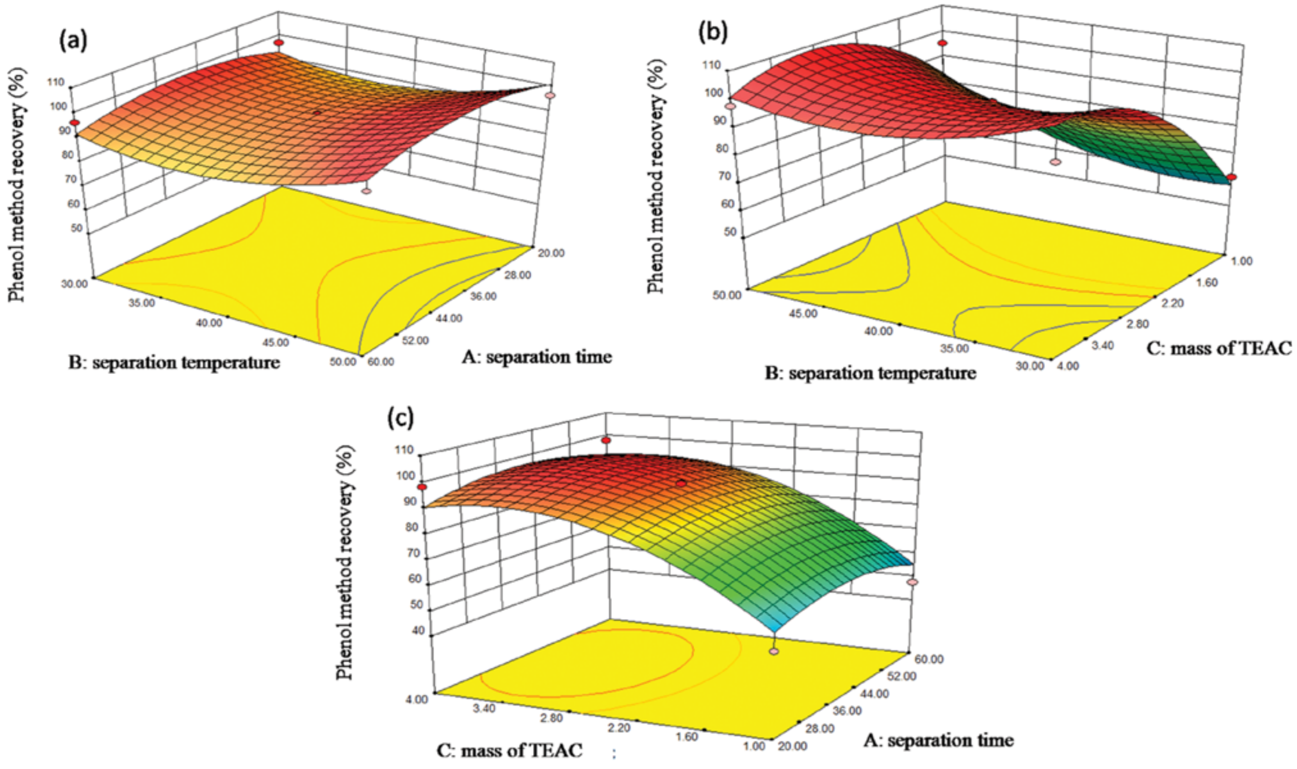

Fig. 8. (a)-(c) Response surface plots showing the effect of separation time (X_1), separation temperature (X_2) and mass of TEAC (X_3) on the method recovery of phenol.

Table 5. Calibration curves (n=5), LODs, and LOQs for phenol

Analytes	Regression equation	R^2	Linear range (μg/mL)	LOD (μg/mL)	LOQ (μg/mL)
Phenol	$Y=1.73\times10^4X-1.57\times10^4$	0.9995	0.5-100.0	0.05	0.17

Table 6. Intra-day and inter-day precision, accuracy and recovery of phenol at three different concentrations (n=3)

	Concentration (μg/mL)	Intra-day		Inter-day		Method recovery (%)
		Measured concentration (μg/mL)	Precision RSD (%)	Measured concentration (μg/mL)	Precision RSD (%)	
Phenol	5.0	4.78	2.35	4.85	2.68	96.3
	50.0	49.56	1.73	49.65	1.98	99.2
	100.0	99.32	1.38	99.49	1.24	99.4

limit of determination (LOD) of phenol was 0.05 μg/mL and the limit of quantitation (LOQ) was 0.17 μg/mL (Table 5). The method recoveries which were determined by repeating the analysis three times and ranged from 96.3 to 99.4%, with the relative standard deviation (RSD) less than 2.68% (Table 6). These results show that the proposed method was stable with wide potential applicability.

CONCLUSIONS

Some quaternary ammonium salts with different structures were successfully used to separate phenol from model oil. The method of separating phenol from oil was obtained by forming DESs (salt/phenol). The results showed that cations with appropriate chain lengths and high symmetry and anions with higher electronegativity were advantageous for the separation phenol from model oil. TEAC showed the best phenol recovery in model oil. Importantly, TEAC can be easily recovered by diethyl ether as an anti-solvent and reused for separating phenol. The optimal separation condition was obtained by RSM at 30 °C for 40 min with 3.75 g TEAC (phenol recovery: 99.3%). In contrast to the traditional methods to separate phenol from oil, this proposed method with the formation of eutectic solvents by quaternary ammonium salt avoids the use of alkalis and acid, and with less effluent.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Optimal separation of phenol from model oils by forming deep eutectic solvents with quaternary ammonium salts

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Table S1. Single factor tests on separation phenol

Factors	Time (min)	Temperature (°C)	Mass of TEAC (g)	Recovery (%)
Time (X_1)	20	40	2	78.60
	60	40	2	88.74
Temperature (X_2)	30	30	1	48.40
	30	50	1	56.35
Mass of TEAC (X_3)	30	40	1	56.35
	30	40	4	95.87

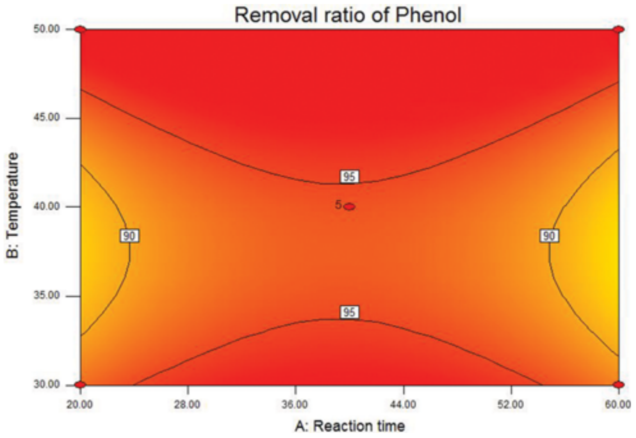

Fig. S1. The effect of reaction time and temperature on recovery.

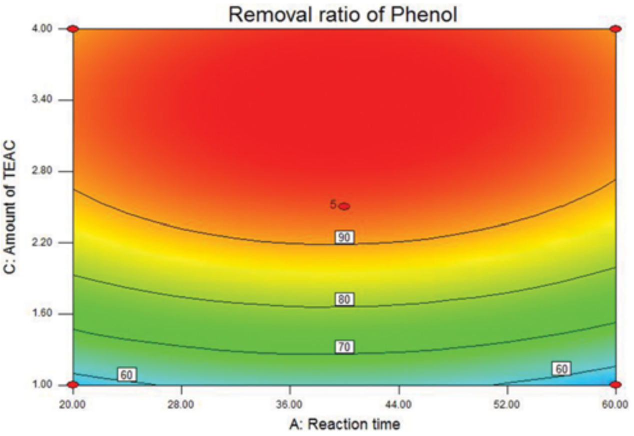

Fig. S2. The effect of reaction time and amount of TEAC on recovery.

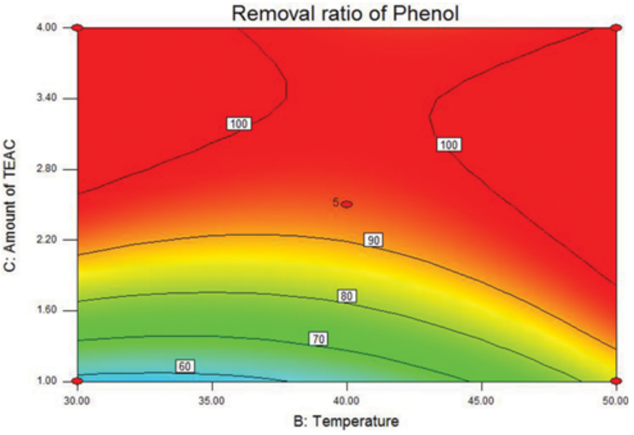

Fig. S3. The effect of temperature and amount of TEAC on recovery.